
Fully Relativistic Description of Static Magnetic Hyperfine Interaction in Magnetic and Nonmagnetic Solids

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ABSTRACT: A fully relativistic description of the static magnetic hyperfine interaction in magnetic solids is presented. This approach is based on a representation of the underlying electronic structure using the Green's function formalism within the framework of relativistic density functional theory. Results for the hyperfine fields in the magnetic alloy $\text{Fe}_x\text{Pd}_{1-x}$ are presented and the importance of relativistic effects for these are discussed. In addition, first results for the Knight shift of 4d transition metals that have been obtained from a fully relativistic linear response formalism are presented and discussed. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 1246–1253, 1999

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Introduction

Because the hyperfine interaction is extremely short-ranged, and because relativistic corrections to the Schrödinger equation primarily affect electronic wave functions close to the nucleus, it is obvious that relativity may have quite a pronounced impact on the hyperfine interaction even for relatively light elements. This was realized

years ago, and a corresponding proper relativistic description of the hyperfine interaction based on the Dirac equation was introduced by Breit.¹ Since then relativistic influences on the hyperfine interaction have been considered and accounted for on various levels of sophistication within many studies on atoms and molecules.^{2–5}

For solids, on the other hand, the situation is quite different. Most calculations of hyperfine fields in spontaneously magnetized solids account just for the enhancement of the matrix elements of the Fermi contact interaction operator due to so-

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called scalar relativistic corrections.⁶ Although the spin-orbit coupling has very important consequences for the hyperfine interaction in solids it is—apart from some few exceptions^{7–9}—normally ignored because of the various technical problems connected with it in the case of magnetic systems. Concerning the static magnetic hyperfine interaction in nonmagnetic solids—represented by the Knight shift—the situation is even worse. So far, there are only some few nonrelativistic investigations that properly account for all contributions to the Knight shift.^{10,11} Concerning a proper and complete relativistic description for the Knight shift only the first steps have been made so far.^{12,13}

In this study, a very flexible approach for a fully relativistic description of the electronic structure of solids within the framework of density functional theory (DFT) is presented. The calculation of the static hyperfine interaction parameters, hyperfine field, and Knight shift for magnetic and nonmagnetic solids, respectively, on this basis is described. In discussing corresponding results for the hyperfine field the importance of relativistic effects is emphasized. First, results for Knight shift calculations demonstrate the feasibility of the proposed approach and the importance of orbital contributions.

Theoretical Framework

ELECTRONIC BAND STRUCTURE CALCULATIONS

Within electronic band structure calculations for solids there are various schemes in use that account for relativistic effects on quite a different level. The most simple one includes just the so-called scalar relativistic corrections; that is, the Darwin and the mass-velocity terms.¹⁴ A simple way to include spin-orbit coupling in addition is to treat it as a perturbation within the variational step of a standard band structure scheme.¹⁵ Obviously, the most satisfying way to deal with all relativistic effects is to use the single-electron Dirac equation:

$$\left[\frac{c}{i} \vec{\alpha} \cdot \vec{\nabla} + \frac{1}{2} c^2 (\beta - I) + V(\vec{r}) \right] \Psi(\vec{r}, E) = E \Psi(\vec{r}, E) \quad (1)$$

within the framework of density functional theory (DFT). This approach is adopted here. In eq. (1), the 4×4 matrices α_i and β are the standard Dirac matrices and Ψ is a four-component wave func-

tion.¹⁶ The effective potential, V , contains, beside the electrostatic Hartree or Coulomb part, a contribution, V_{xc} , that represents all exchange and correlation effects. If one is dealing with spontaneously magnetized solids, it is standard to construct V_{xc} on the basis of the relativistic version of spin density functional theory (SDFT).¹⁷ This implies that V_{xc} contains a spin-averaged part, \bar{V}_{xc} , and a spin-dependent part, V_{spin} , that is given by¹⁷:

$$V_{spin} = \beta \vec{\sigma} \cdot dE_{xc}/d\vec{m} \quad (2)$$

Here, E_{xc} is the exchange correlation energy and \vec{m} stands for the spin magnetization density. In recent years several approaches have been suggested to go beyond spin density functional theory aiming in particular to account for the orbital contributions to the magnetization. Here, one should first mention the Brooks orbital polarization scheme,¹⁸ and the more rigorous current density functional theory (CDFT) developed by Vignale and Rasolt.¹⁹ Although most of the work presented in what follows has been done in the framework of SDFT, reference will be made to these schemes where substantial corrections are to be expected.

For most of the many different band structure methods based on the variational principle a corresponding relativistic version is available that is based on the previously noted Dirac equation (at least for the nonmagnetic case for which $V_{spin} = 0$). A much more general and flexible description of the electronic structure of a solid is achieved by using the Green's function formalism. Using multiple scattering, or the Korringa-Kohn-Rostoker (KKR) techniques, the corresponding Green's function, $G(\vec{r}, \vec{r}', E)$, is given by²⁰:

$$G(\vec{r}_n, \vec{r}_m, E) = \sum_{\Lambda \Lambda'} Z_{\Lambda}^n(\vec{r}_n, E) \tau_{\Lambda \Lambda'}^{nm}(E) Z_{\Lambda'}^m(\vec{r}_m, E) - \sum_{\Lambda} Z_{\Lambda}^n(\vec{r}_n, E) J_{\Lambda}^n(\vec{r}_n, E) \delta_{nm} \quad (3)$$

Here, the functions Z_{Λ}^n and J_{Λ}^n are the regular and irregular solutions to the Dirac equation for an isolated potential well centered on site n . These functions are labeled by the set of relativistic quantum numbers $\Lambda = (\kappa, \mu)$ with κ and μ the spin-orbit and magnetic quantum numbers, respectively. Here one must note that Λ denotes the spin-angular character of the functions Z_{Λ}^n and J_{Λ}^n only for the case of a spherical symmetric potential¹⁶ as it occurs, for example, within a muffin-tin or atomic-sphere (ASA) construction. If one allows the potential to be anisotropic, then Λ gives just the asymptotic behavior of the wave functions that

are, in general, a superposition of various contributions; for example, $Z_{\Lambda}^n = \sum_{\Lambda'} Z_{\Lambda'\Lambda}^n$. This also applies to a spin-polarized or magnetic system for which the term V_{spin} breaks symmetry in spin space. As a consequence, only μ is left as a good quantum number, whereas partial waves of the same parity, but different κ , get mixed.

Finally, $\tau_{\Lambda\Lambda'}^{nm}$ in eq. (3) is the scattering path operator. This operator transfers a wave with spin-angular character Λ' coming in at site m into a wave outgoing from site n with character Λ and with all possible scattering events that may take place in between accounted for. For an ordered system with one atom per unit cell, $\tau_{\Lambda\Lambda'}^{nm}$ is obtained from the Brillouin-zone integral:

$$\tau_{\Lambda\Lambda'}^{nm}(E) = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d^3k \left[t^{-1}(E) - \underline{G}(\vec{k}, E) \right]_{\Lambda\Lambda'}^{-1} \times e^{i\vec{k}(\vec{R}_n - \vec{R}_m)} \quad (4)$$

Here, $\vec{R}_{n(m)}$ denotes the lattice vector for site $n(m)$, t is the single-site t -matrix and \underline{G} is the relativistic structure constant matrix representing free electron propagation between the scattering centers. For more complex systems, corresponding schemes are available to calculate $\tau_{\Lambda\Lambda'}^{nm}$ as well. In particular, this calculation can also be done using a real space formulation without making use of any spatial ordering of the scatterers or atoms.²¹

The KKR method was originally developed by Korringa²² and Kohn and Rostoker²³ to deal with the itinerant electronic states in ordered systems. These investigators used the free electron Green's function to set up an integral equation corresponding to the original Schrödinger equation (Lippmann-Schwinger equation) and to derive a secular equation from this by application of the variational principle. This formalism was later used by Slater and Johnson²⁴ to deal with the bound electronic states in a molecule when setting up the $X\alpha$ multiple-scattering method. During the 1970s, the KKR band-structure method was extended by many investigators, such as Beeby,²⁵ Harris,²⁶ and Györffy and Stott,²⁷ to calculate the single-electron Green's function directly instead of calculating Bloch functions and eigenvalues. This feature has been exploited in particular when dealing with disordered alloys in connection with the coherent potential approximation (CPA) alloy theory (see later). Dealing with paramagnetic solids on the basis of the Dirac equation is quite straightforward and, accordingly, a corresponding version of the original KKR method had already been developed in the

1960s by Onodera and Okazaki.²⁸ The necessary formalism to allow addition of spin polarization has been worked out only as recently as the beginning of the 1980s, by Feder et al.²⁹ and Strange et al.³⁰ Originally, the KKR method was formulated, like Slater's APW method, by making use of the muffin-tin construction for the charge and the potential. Later, the ASA, which also assumes spherical symmetry, was used as well because of its numerical convenience. A consistent full-potential (FP) version of the nonrelativistic KKR method was first introduced by Dederichs et al.³¹ by expanding charge and potential within an atomic cell in spherical harmonics. This approach has recently been combined with the spin-polarized relativistic (SPR) version of the KKR method.³² Common to all these recent versions of the KKR method is that they account for nonspherical parts of the potential and/or the spin-orbit coupling already when calculating the corresponding electronic wave functions, Z_{Λ} , which are, for that reason, generally a superposition of several contributions (see earlier). Thus, due to its numerical accuracy the FP (SPR) KKR method is superior to conventional band structure methods. For these methods it is common to construct the corresponding basis functions from wave functions calculated for a spherical potential and ignoring the spin-orbit coupling. Nonspherical potential terms and/or spin-orbit coupling are then accounted for only within the variational step. However, in practice, results based on these two rather different approaches scarcely differ. Thus, it is primarily the great flexibility of the KKR method, particularly when dealing with disordered alloys, systems without translational symmetry, or calculating response functions, that has motivated its use here. Because for the closely packed solids investigated here, nonspherical potential terms can be ignored,³² all calculations have been done using the ASA.

HYPERFINE INTERACTION OPERATOR

The magnetic hyperfine interaction operator, H_{hf} , represents the interaction of the nuclear magnetic moment, $\vec{\mu}_n$, with the current density, \vec{j} , of the surrounding electronic system. In its relativistic form, H_{hf} is given by^{16,33}:

$$H_{hf} = ec\vec{\alpha} \cdot \vec{\mu}_n \times \vec{r}/r^3 \quad (5)$$

In what follows, only the static part of the hyperfine interaction is considered, assuming that the magnetization and quantization axis points along

the z -axis. Accordingly, only the $H_{hf,z} \propto \alpha_z (\vec{\mu}_n \times \vec{r})_z$ part has to be accounted for.

Within a nonrelativistic theoretical description of the hyperfine interaction it is conventional to split the total hyperfine interaction operator into three distinct contributions: the Fermi contact; the spin-dipolar; and orbital terms. Whereas the first is relevant only for s -electrons, the other two are connected exclusively to non- s -electrons. Starting from a Gordon decomposition of the electronic current, a corresponding decomposition of the hyperfine interaction operator, H_{hf} , in eq. (5) can also be made within relativistic theory.^{5,34,35} For the orbital part, one gets, for example, the expression:

$$H_{hf,orb} = 2\mu_B \beta \vec{\mu}_n \vec{l} \cdot \begin{cases} r^{-3} & \text{for } r > r_n \\ r_n^{-3} & \text{for } r < r_n \end{cases} \quad (6)$$

where r_n is the nuclear radius. This expression already indicates that, for the decomposition of the relativistic hyperfine interaction operator, a nucleus of finite size has to be considered.^{5,35} Furthermore, one must note that the various parts of H_{hf} are no longer exclusively due to s - or non- s -electrons, respectively.

HYPERFINE FIELDS IN SPONTANEOUSLY MAGNETIZED SOLIDS

For spontaneously magnetized solids, the central hyperfine interaction parameter is the hyperfine field B_{hf} . This quantity is determined by the expectation value of the static part of the hyperfine interaction operator:

$$B_{hf} = \langle H_{hf,z} \rangle / \hbar \gamma_n \quad (7)$$

with γ_n the nuclear gyromagnetic ratio. Representation of the underlying electronic structure by means of the Green's function formalism $\langle H_{hf,z} \rangle$, in turn, is given by⁷:

$$\langle H_{hf,z} \rangle = -\frac{1}{\pi} \text{Trace} \oint dE \int d^3r H_{hf,z}(\vec{r}) G(\vec{r}, \vec{r}, E) \quad (8)$$

Dealing with this expression on a nonrelativistic level one gets contributions to the hyperfine field, B_{hf} , only from the Fermi contact and spin-dipolar terms, because the orbital magnetization density is quenched in the solid.³⁶ Contributions due to the spin-dipolar term are in general ignored because they arise only from a noncubic electronic spin density distribution. Therefore, the standard ap-

proach to calculate hyperfine fields is to determine only its Fermi-contact contribution stemming from s -electrons. In contrast to this simple but conventional approach, the fully relativistic scheme just given leads to contributions to the hyperfine field from non- s -electrons as well. These are caused by the spin-orbit coupling and are nonnegligible even for cubic systems.⁸

KNIGHT SHIFT IN NONMAGNETIC SOLIDS

The conventional approach to deal with the Knight shift in nonmagnetic solids is to use perturbation theory with Bloch wave functions as the unperturbed wave functions.³⁷ A more flexible approach is to use the previously noted Green's function technique together with linear response formalism. In close analogy to eq. (7), the Knight shift can be expressed by:

$$K = \langle H_{hf,z} \rangle / \hbar \gamma_n B_{ext} \quad (9)$$

where $\langle H_{hf,z} \rangle$ must be determined from a Green's function, $G^B(\vec{r}, \vec{r}', E)$, which accounts for the presence of an external magnetic field, B_{ext} . Using first order approximation to the Dyson equation for G^B one obtains:

$$G^B(\vec{r}, \vec{r}', E) = G(\vec{r}, \vec{r}', E) + \int d^3r'' G(\vec{r}, \vec{r}'', E) H_{pert}^{spin}(\vec{r}'') \times G(\vec{r}'', \vec{r}', E) \quad (10)$$

where H_{pert}^{spin} is the perturbation operator representing the effect of the external field. If the aforementioned expansion is made for a nonmagnetic solid, the Green's function, $G(\vec{r}, \vec{r}', E)$, representing the unperturbed system does not contribute when eq. (10) is inserted into eq. (8). Accordingly, the Knight shift is connected only to the second term in eq. (10). If one assumes that the external field couples only to the spin of the electron, H_{pert}^{spin} is given within SDFT by two terms:

$$H_{pert}^{spin} = \sigma_z [2\mu_B B_{ext} - (V_{xc}^\uparrow - V_{xc}^\downarrow)] \quad (11)$$

The second term represents a feedback of the induced spin magnetization via the modified exchange and correlation potential. Calculating the spin susceptibility, χ_{spin} , along the same line, this term gives rise to the so-called Stoner enhancement factor, S , that can assume quite high values (e.g., $S \approx 10$ for Pd³⁸). Of course, the same enhancement mechanism increases the contribution

to the Knight shift due to H_{pert}^{spin} compared with a calculation ignoring the modified electron–electron interaction.

In addition to the spin an external magnetic field couples also to the orbital degree of freedom of the electrons. Concerning the magnetic susceptibility this gives rise to the conventional Langevin and Landau diamagnetic and the Van-Vleck paramagnetic contributions.³⁹ Of these, only the Langevin and the Van-Vleck parts have a counterpart involving the Knight shift.¹⁰ The latter one can be calculated, as described earlier, with H_{pert}^{spin} replaced by:

$$H_{pert}^{orb} = 2\mu_B l_z B_{ext} \tag{12}$$

As for eq. (11), one has, in principle, to account also for the modified electron–electron interaction by an additional term that can be formulated, for example, within CDFT (see earlier). Similar to the Stoner enhancement mechanism this should give rise to a quite appreciable influence on the Knight shift.⁴⁰ In spite of this expectation this mechanism has been neglected so far due to various technical problems.

Finally, one should note that there is a fundamental difference between the relativistic linear response formalism outlined here and its nonrelativistic counterpart.¹⁰ In the relativistic case, it is no more possible to distinguish properly spin and orbital contributions. The reason for this is that, as a consequence of the spin–orbit coupling, H_{pert}^{spin} gives rise to a spin but also to an orbital contribution to K via the hyperfine interaction operator H_{hf} . The same applies to the orbital perturbation operator H_{pert}^{orb} .

Applications to Transition Metal Systems

HYPERFINE FIELDS IN DISORDERED ALLOY SYSTEM $\text{fcc-Fe}_x\text{Pd}_{1-x}$

In what follows, applications of the previously discussed relativistic scheme to calculate the hyperfine fields in disordered $\text{fcc-Fe}_x\text{Pd}_{1-x}$ alloys is presented. Such an investigation is possible because the Green’s function formalism combined with a suitable alloy theory allows one to deal with chemically disordered systems. For this purpose the coherent potential approximation (CPA) is used, which is the best alloy theory that can be set up on a single-site level.

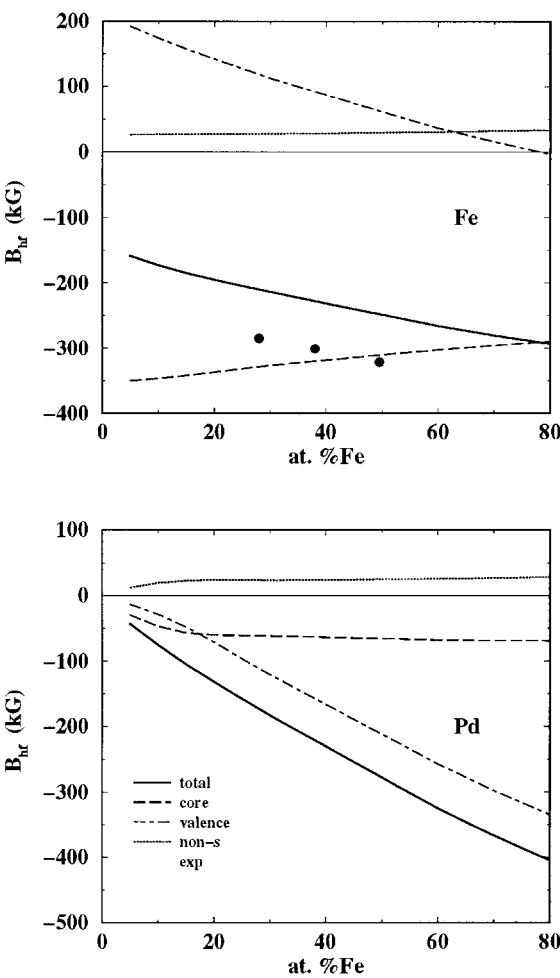


FIGURE 1. Hyperfine fields of Fe (top) and Pd (bottom) in $\text{fcc-Fe}_x\text{Pd}_{1-x}$. In addition to the total field, $B_{hf}(\text{total})$ the contributions of the core, valence, and non-s-electrons are given separately. For Fe available experimental data have been added.

Figure 1 shows the total hyperfine fields of Fe and Pd in $\text{fcc-Fe}_x\text{Pd}_{1-x}$, together with a decomposition into contributions stemming from the core, valence, and non-s-electrons. The experimental data available for Fe indicate that the theoretical fields are too small in magnitude. Discrepancies similar to this have been found before for many other systems and have been ascribed to problems in dealing with the core polarization contribution when the spin density functional theory is used on a local density approximation (LDA) level.^{6,7} However, improvements to the LDA, like the generalized gradient approximation (GGA)⁴¹ or the self-interaction correction (SIC),^{41,42} did not give much better results. By using the optimized effective potential (OEP), on the other hand, very satisfying

results for the hyperfine fields of Fe, Co, and Ni can be achieved.⁴³

Within a nonrelativistic calculation of the hyperfine fields in $\text{Fe}_x\text{Pd}_{1-x}$ one would get only contributions due to the s-electrons via the Fermi-contact interaction. Within a fully relativistic investigation this part is enhanced by about 10% (20%) for Fe (Pd).⁸ In addition, one finds quite appreciable contributions from non-s-electrons. These are induced by the spin-orbit coupling and are, in general, opposite to the normally dominating negative core polarization fields.

The dominating part of the non-s-fields stemming from the valence band electrons is given once more in Figure 2 in an angular-momentum

resolved way. For Fe the p-contribution is very small and has been omitted for that reason. For Pd, on the other hand, it may take up to 50% of the d-contribution. With the proper relativistic decomposition of the hyperfine interaction in eq. (5) the origin of these fields can be investigated in a detailed way. The corresponding fields, $B_{orb,p}$ and $B_{orb,d}$, obtained using the relativistic orbital hyperfine interaction operator [see eq. (7)] have been added to Figure 2. As one can see these fields differ only slightly from $B_{val,p}$ and $B_{val,d}$, respectively implying that the fields coming from the p- and d-electrons via the Fermi contact and spin dipolar interaction are, in general, neglectable. This is also confirmed by an additional calculation of these fields. Thus, it is quite justified to call the spin-orbit-induced hyperfine fields coming from non-s-electrons—in a somewhat loose way—*orbital*.⁸

One of the most important consequences of the spin-orbit coupling for magnetic solids is that the orbital angular momentum is not completely quenched. This implies the presence of a spin-orbit-induced orbital electronic current density that gives rise to, according to eq. (5), the relativistic hyperfine fields discussed earlier. In addition, it causes a corresponding orbital contribution, μ_{orb} , to the total magnetic moment. Because of their common physical origin one can expect the fields, B_{orb} , and the moment, μ_{orb} , to be related via⁴⁴:

$$B_{orb,l} = 2\mu_B \langle r^{-3} \rangle \mu_{orb,l} \quad (l = p, d) \quad (13)$$

As can be seen in Figure 2, this simple approximation works quite well, justifying once more use of the designation *orbital*.

KNIGHT SHIFT OF PURE 4D-TRANSITION METALS

As mentioned earlier, there are only very few theoretical investigations on the Knight shift in transition metal systems that can be found in the literature. Very similar to the situation for the hyperfine field of spontaneously magnetized solids nearly all of these considered only the Fermi-contact interaction for the s-electrons. Using a nonrelativistic version of the linear response formalism presented earlier, the first calculation of all contributions to the Knight shift has been done for the transition metals V, Cr, Nb, and Mo.¹⁰ For these metals, the Van-Vleck contribution to the magnetic susceptibility and to the Knight shift was found to

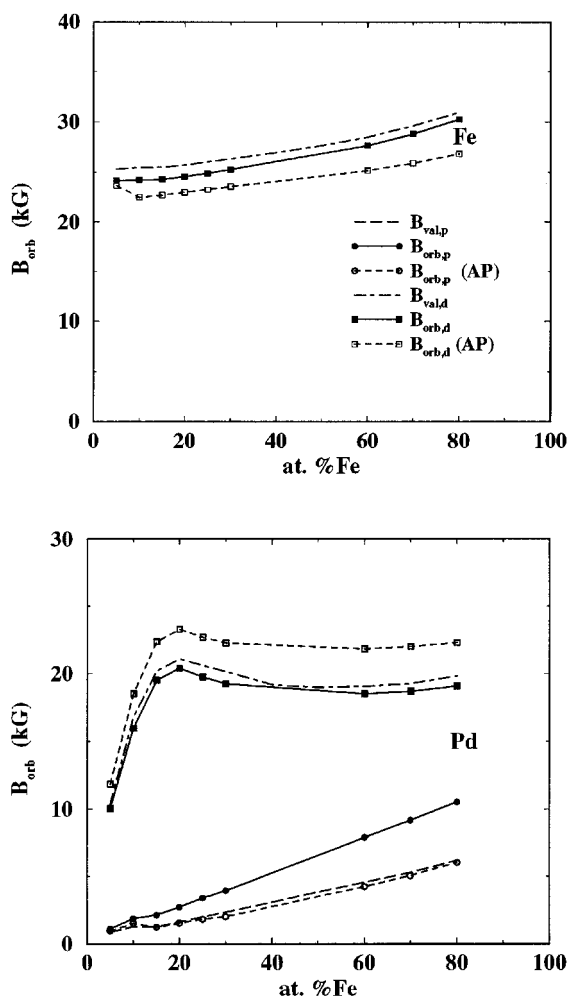


FIGURE 2. Contributions B_{val} of the d-like valence electrons to the hyperfine fields of Fe (top) and Pd (bottom) in fcc- $\text{Fe}_x\text{Pd}_{1-x}$. The fields B_{orb} represent the corresponding orbital part. This has also been determined by the approximation due to Abragam and Pryce [AP; see eq. (13)].⁴⁴ For Pd, the data for the p-electrons are given in addition.

be of the same order of magnitude as the various spin contributions and to stem nearly exclusively from the d-electrons. Concerning magnetic susceptibility similar results have been obtained by Yasui and Shimizu using a nonrelativistic⁴⁵ as well as a fully relativistic⁴⁶ approach.

Initial results obtained using the aforementioned relativistic linear response formalism are given in Figure 3. The top panel of this figure shows the Van-Vleck susceptibility, χ_{VV} , of the pure 4d-transition metals. As found within earlier studies a maximum was found for χ_{VV} roughly in the middle of the row. This can be explained by using a simplified expression for χ_{VV} ³⁷ and the fact that here the product ($n_o \cdot n_u$) of the number of occupied (n_o) and unoccupied (n_u) d-states is maximal. From the relationship of the orbital parts of the magnetic moment and the hyperfine field [see eq. (13)] one can expect an analogous relationship for the Van-Vleck contributions to the susceptibility and Knight shift:

$$K_{VV,l} = 2\mu_B \langle r^{-3} \rangle \chi_{VV,l} \quad (l = p, d) \quad (14)$$

As one can see in Figure 3 (middle), the expectation value $\langle r^{-3} \rangle_d$ for the 4d elements increases rapidly along the 4d row. The reason for this is that the corresponding d-like wave function gets more and more localized with increasing atomic number. Combining the results for χ_{VV} and $\langle r^{-3} \rangle_d$ using eq. (14) leads to an estimate for the Van-Vleck Knight shift K_{VV} is shown in Figure 3 (bottom). Due to the variation of $\langle r^{-3} \rangle_d$ the maximal K_{VV} is obviously shifted to the right compared with the χ_{VV} curve. Figure 3 shows, in addition, the K_{VV} shift that has been obtained by using the full formalism; that is, eqs. (6), (9), (10), and (12). As one can see, the estimation of K_{VV} using χ_{VV} and $\langle r^{-3} \rangle_d$ reproduces the variation with atomic number quite well. However, in line with previous nonrelativistic results,¹⁰ the absolute values differ by up to about 20%. This means that estimation based on Eq. (14) are generally less reliable than spin-orbit-induced orbital hyperfine fields estimated using eq. (13).

Finally, it should be emphasized that the Van-Vleck Knight shift, K_{VV} , given in Figure 3, stems from the coupling of the external magnetic field to the orbital degree of freedom [see eq. (12)]. Because of the use of the relativistic orbital hyperfine interaction operator [see eq. (6)] it is, by definition, of pure orbital nature. If the full hyperfine interaction operator [eq. (5)] is used instead, the Knight shift, denoted K_{val} in Figure 3, is obtained. The

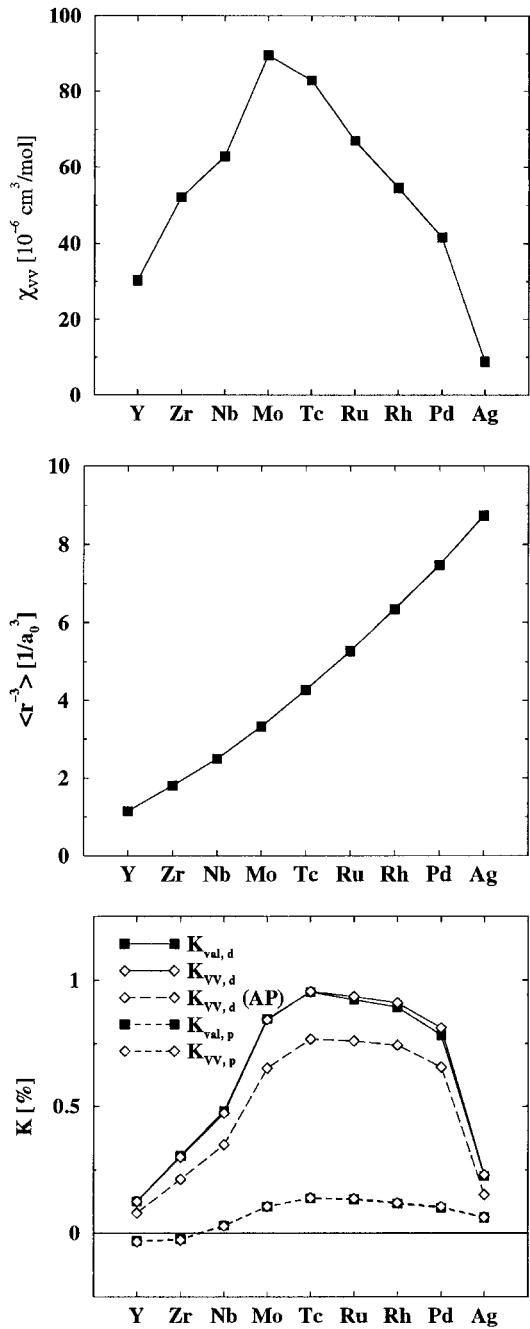


FIGURE 3. Van-Vleck susceptibility χ_V (top), expectation value of r^{-3} (middle), and Van-Vleck contribution to the Knight shift K_{VV} (bottom) for the d-valence-band electrons of the pure 4d-transition metal elements. The estimation for K_{VV} , based on the approximation proposed by Abragam and Pryce (AP) as well as the total valence contribution K_{val} due to the orbital perturbation term H_{pert}^{orb} in eq. (12), has been added (bottom).

small difference between K_{vv} and K_{val} is of pure spin nature. Within a nonrelativistic formalism this cross-contribution cannot be accounted for, because it is a consequence of spin-orbit coupling.

Summary

A very general approach has been presented that allows one to deal with the hyperfine interaction in magnetic and nonmagnetic solids in a consistent and fully relativistic way. Results presented for the magnetic alloy system, $\text{Fe}_x\text{Pd}_{1-x}$, demonstrated in particular that spin-orbit coupling, which is usually ignored, gives rise to nonnegligible contributions to the hyperfine field, even for relatively light elements. A first application of the proposed approach to nonmagnetic solids allowed the calculation of the Van-Vleck contributions to the Knight shift of 4d-transition metals that were found to be quite large and that are nevertheless usually ignored. For the magnetic as well as the nonmagnetic case the close connection between the quantities representing the global magnetic properties—magnetic moment and susceptibility, respectively—to the local hyperfine parameters—hyperfine field and Knight shift, respectively—can be revealed.

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